

# PATENT SPECIFICATION

DRAWINGS ATTACHED

970.945



970.945

Date of Application and filing Complete Specification Sept. 22, 1961.

No. 34011/61.

Application made in Italy (No. 19,676) on Nov. 12, 1960.

Complete Specification Published Sept. 23, 1964.

© Crown Copyright 1964.

Index at acceptance: —C2 C(3A13B2A1, 3A13B2E, 3A13B2F3, 3A14A1A, 3A14A6, 3A14A7A)

International Classification:—C 07 c

## COMPLETE SPECIFICATION

### Process for Neutralising Acidic Acetone-phenol Mixtures

We, SOCIETA' ITALIANA RESINE, an Italian body corporate, of 33, via Grazioli, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that acidic cleavage or hydrolysis of pure or dilute cumene hydroperoxide yields phenol and acetone. The acidic cleavage reagents employed in the hydrolysis or cleavage are normally non-oxidising inorganic acids, such as sulphuric and/or hydrochloric acid, the cleavage usually being performed on an "oxidate" containing from 20 to 90% by weight cumene hydroperoxide, the balance consisting essentially of cumene and its decomposition products formed during the oxidising reaction, such as acetophenone and dimethyl or phenylcarbinol.

While still acidic the hydrolysis mixtures cannot be conveyed to the subsequent rectifying columns, for the free acid therein would give rise to serious corrosion problems.

Neutralisation of the acidic hydrolysis mixtures of cumene hydroperoxide is normally effected by means of caustic soda, sodium carbonate or sodium phenolate solutions.

The acid employed for hydrolysis of cumene hydroperoxide is effectively neutralized in this manner, but, at the same time, serious drawbacks arise in the subsequent fractionations for recovery of phenol and acetone.

The inorganic salts formed, such as sodium sulphate, remaining in the neutralised mixture tend to separate, thereby obstructing lines, and choking reboilers, while sodium salts of the carboxylic acids contained in the cumene hydroperoxide solution decompose under the action of heat during distillation and the resulting by-products contaminate more particularly the acetone which does not meet therefore the standard purity tests.

In order to obviate in part at least the above drawbacks it was suggested to separate from the neutralised hydrolysis mixture a fraction containing most of said alkali metal salts and to wash the mixture with pure water.

While washing removes in part at least the abovementioned difficulties, it entails a considerable loss of acetone and phenol which dissolve in the washing water and can only be recovered with difficulty, which is more particularly true of phenol on account of the low concentrations and characteristics of the phenol water distillation curve. This necessitates elaborate solvent-extraction processes.

This invention provides a novel method of neutralising acidic mixtures produced by the acidic hydrolysis of an oxidate containing at least 25% by weight cumene hydroperoxide whether side-products of oxidation of cumene air or molecular oxygen, such as acetophenone and dimethylphenylcarbinol are present or not, by simply causing the mixture to flow over anion-exchange resin of the anion type. The resin is advantageously contained in a suitable column.

It is surprising that sulphuric acid and other inorganic acids used for the acidic cleavage of oxidates containing at least 25% by weight cumene hydroperoxide can be thoroughly removed over anion exchange resins from substantially non-aqueous solutions in the presence of phenol.

The advantages afforded by the above procedure can be summarized as follows:

1) total absence in the effluent from the neutralising plant of inorganic or organic alkali and alkaline-earth salts which could settle-out in the reboilers in the rectification columns;

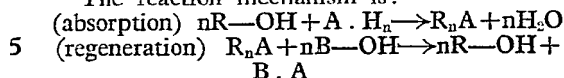
2) the water content in the effluent is not increased with respect to supply, which is of a considerable advantage in the rectification of the various products therein contained;

3) valuable products, such as acetone and

[P]

phenol contained in the hydrolysis mixture are wholly retained by the effluent.

The reaction mechanism is:



as is known in the art.

Conventional anion exchange resins are suitable for neutralising the solutions from the hydrolysis of cumene hydroperoxide according to this invention.

Phenolic-base resins having secondary-amino and tertiary-amino functional groups are preferred. Examples of such resins are "Duolite" A7 and "Duolite" A2 manufactured by Chemical Process Co., Redwood City, California, or other resins of similar properties "Duolite" is a trade mark).

Before supply of the acidic liquid to be neutralised is started, the resin should be brought to its hydroxide form by a conditioning treatment with dilute caustic soda solution, whereupon excess caustic soda is removed by means of distilled or demineralized water and residual water in the resin is washed out with acetone until the water has been completely displaced. A fixed bed of resin in a column is advantageously employed.

The acetone in the dilute aqueous solution resulting from the above washing is recovered by distillation for re-use.

In industrial practice the dilute acetone solution is conveyed to the purifying column in which the raw acetone recovered from the hydrolysis mixture is also purified.

When the water has been fully displaced from the resin the acetone supply is stopped and the supply of the acidic hydrolysate to be neutralised is started.

When the resin is spent, the supply of the acidic hydrolysate is stopped, and the residual partly-neutralised hydrolysate in the resin is displaced by acetone, the resulting mixture being added to the acidic hydrolysate to be neutralised in the next run.

Upon completion of the above displacement, the acetone is displaced in turn by demineralized or distilled water, the resulting dilute acetone being added to the dilute acetone previously obtained during the resin-conditioning step.

At this stage conventional regeneration of the resin by means of a sodium hydroxide solution is effected, whereupon the cycle is repeated.

The above described working cycle can be modified as follows.

Upon washing the resin bed with water after regeneration with caustic soda, instead of displacing the residual water in the resin with acetone as described above, the water is discharged from the resin bed simply by draining.

Water absorbed by the resin is removed

by a warm air stream at a temperature which will not damage the resin, this temperature generally does not exceed 45—50° C.

When the moisture content in the air at the outlet is identical to that at the air inlet the resin is sufficiently dehydrated; the air supply is stopped and supply of the mixture to be neutralised is started.

Upon completion of the cycle instead of displacing the residual semi-neutralised mixture in the resin by means of acetone as previously described, the mixture is drained from the neutralization column with the assistance of compressed air for improving exhaustion and purging the bed.

Upon discharge of the mixture, an acetone quantity slightly exceeding the volume of the resin is introduced three times into the column from the bottom of the latter, the washing acetone being discharged in each instance from the bottom of the column.

Upon completion of the last washing step by means of acetone, a similar volume of demineralized or distilled water is supplied from the bottom.

The aqueous acetone solution formed is likewise discharged from the bottom and conveyed to the acetone distillation apparatus mentioned above.

Water-washing and regeneration steps are thereafter effected.

The enclosed drawing diagrammatically shows an apparatus for carrying out this invention.

The apparatus comprises a column 10 the lower half of which contains a bed 11 of anion-exchange resin.

The bed is supported on a porous septum 14 and a further porous septum 12 is arranged between the bed and the top of the column.

Tanks 15 and 16 are arranged above the column and connect with a top section of the latter through conduits 17, 18, respectively, equipped with control valves 19, 20, respectively.

In operation, tank 15 contains a sodium hydroxide solution, whereas acidic hydrolysate is contained in the tank 16.

Demineralized or distilled water can be supplied to the column either through a conduit 21 equipped with a control valve 22 opening into the top section of the column, or through a conduit 21a equipped with a control valve 22a opening into the bottom section of the column beneath porous septum 14.

Further two conduits, denoted by 23 and 24 open into the top section of the column via control 25, 26, respectively, for supplying to the column acetone and warm air (45°—50° C) respectively.

A discharge conduit 28 ending by a three-way valve 29 extends from the bottom of the column, the valve 29 being adapted to selec-

tively control connection of the conduit 28 with conduits 30, 31 and 32.

Conduits 30 leads to a rectification apparatus (not shown) for aqueous acetone solution discharged from the column.

Conduit 31 leads to waste, and conduit 32 is an outlet conduit for hydrolysate out-flowing from the column.

The conduit 32 ends by a two-way valve 33 for a selective connection of the conduit with conduits 34, 35 extending from the valve.

Fully neutralized hydrolysate is discharged through the conduit 34 to stockage; part-neutralized hydrolysate is recirculated through conduit 35 to the tank 16.

A conduit 36 having a control valve 37 interposed therein opens into a bottom section of the column beneath the lower porous septum 14 for purging the resin bed with acetone.

A discharge conduit 38 controlled by a valve 39 extends from the top section of the column.

The following examples are explanatory of the invention but should not be understood as limitations thereof.

#### EXAMPLE 1

An apparatus is employed substantially as shown on the drawing. The column 10 has an inner diameter of 3.0 cm. and the distance between the porous septa 12, 14 is 100 cm. The volume enclosed between the septa is thus  $\sim 700 \text{ cm}^3$ . The volume of the resin bed 11 is  $350 \text{ cm}^3$ , the resin consisting of "Duolite" A7 in acidic condition.

Valves 22a and 39 are open and the resin bed is washed in upward direction with distilled water supplied at a rate 3.5 liters/hour.

After 15 minutes of washing, valves 22a and 39 are closed and 7.5% by weight NaOH solution from tank 15 is allowed to descend through the column *via* valves 19, 29 to waste 600 ml. solution flowing at a rate 1.75 liters/hour are sufficient to regenerate the resin in about 20 minutes.

A downward washing of the resin by distilled water is then performed by closing the valve 19 and opening valve 22; washing water is caused to descend through the column at the NaOH-rate (1.75 liters/hour) for first 20 minutes, thereafter the flow rate is increased to 4 litres/hours and is pursued till litmus-neutral effluent is reached in conduit 31.

The initial effluent will contain sodium sulfate and chloride, thereafter sodium hydroxide will temporarily appear in the effluent instead of the above salts and, ultimately, the effluent will consist of distilled water.

Water retained by the bed is displaced by a downward flow of acetone at a rate 0.7 liters/hour and the thirteen-minutes effluent (150 ml) is discharged to waste. The

subsequent twenty-two-minutes effluent (260 ml) is recovered *via* conduit 30 and forwarded to a distillation-rectification apparatus, the effluent consisting of aqueous acetone at about 65% by weight concentration of acetone. At the 36th minute of water-displacement by acetone the effluent is pure acetone.

At this stage acetone washing is stopped and valve 20 is opened whereby acidic hydrolysate flows by gravity into and through the column at a rate 0.7 liters/hour.

The thirteen-minutes effluent (150 ml) is still pure acetone and is recovered. At 14th minute the effluent starts to contain neutralized hydrolysate in continuously increasing proportions and is recovered *via* conduit 32, valve 33 and conduit 34.

After about 29 hours the resin starts exhausting, whereby the valve 33 is switched-over to connect conduit 32 to the re-cycle conduit 35 and valve 20 is closed.

The part-neutralized hydrolysate in the column is now displaced by acetone by opening the valve 25; acetone is supplied at a rate 1.4 liters/hour in a downward flow and the acidic hydrolysate effluent containing acetone is recirculated to the tank 16; after about one hour hydrolysate is displaced from the column, whereupon acetone in the column is displaced by a downward flow of water from conduit 21 at a rate 0.7 liter/hour. The thirteen-minutes effluent (150 ml) is pure acetone; the further twentytwo-minutes effluent (260 ml) is a mixture of acetone and water (about 50% by weight average concentration of acetone) which is forwarded to rectification through conduit 30.

At the 36th minute of water-washing the effluent is pure water. At this stage a subsequent run is started with 15-minute washing with water in upward flow (counter-current) at 3.5 liters/hour, regeneration with 7.5% by weight solution NaOH in downward flow (co-current) at 1.75 liters/hour, washing by downward (co-current) flow of water, and displacement of water by acetone, as described hereinbefore.

The acidic hydrolysis employed both in this Example as well as in following Examples 2—4 was of the following composition, by weight:—

Phenol	-	-	-	-	-	about 36%
Acetone, cumene, acetophenone, dimethylphenylcarbinol	-	-	-	-	-	about 58%
Water	-	-	-	-	-	about 5%
H <sub>2</sub> SO <sub>4</sub>	-	-	-	-	-	0.2%

#### EXAMPLE 2

Upon washing in counter-current, regeneration and washing in co-current, as described in Example 1, the column is emptied by opening the valve 29 to waste.

About 190 ml water are discharged, the remaining water retained by the resin being

displaced by means of an air stream at 45° C.

- 5 When the moisture content in the outflowing air is equal to that in the in-flowing air, the air supply is stopped and the hydrolysate solution is caused to flow downwardly at a rate of 0.7 liters/hour.

The resin is exhausted after 30 hours.

- 10 The column is emptied through valve 29 and conduit 32 with the assistance of compressed air, the discharged mixture being recycled through conduit 35.

- 15 Acetone is then caused to flow in upward flow at a rate of 0.7 liters/hour during 30 minutes, then discharged from the bottom.

This step is repeated three times totalling about 1.1 liters acetone.

- 20 Upon discharge of the acetone of the last washing, water is caused to flow in upward flow (counter-current) at a rate of 0.7 liters/hour for 20 minutes.

- 25 The aqueous acetone solution containing 40% by weight acetone is discharged from the bottom via conduit 30 and conveyed to acetone-recovery apparatus.

The resin is then regenerated as in Example 1 for a subsequent run.

#### EXAMPLE 3

- 30 A "Duolite" A2 exchange resin is used. The steps are carried out as described in Example 1. The resin becomes exhausted after 24 hours instead of 29 hours on account of the lower exchange capacity of A2 resin with respect to the A7 grade.

#### EXAMPLE 4

- 35 "Duolite" A2 exchange resin is used similarly to Example 3.

The same steps as described in Example 2 are carried out.

- 40 The resin becomes exhausted after 25 hours instead of 30 hours for the reason explained in Example 3.

#### WHAT WE CLAIM IS:—

1. A method of neutralising the phenol and acetone-containing acidic hydrolysate obtained by the hydrolysis of solutions of cumene hydroperoxide in cumene containing at least 25% by weight of cumene hydroperoxide, with inorganic acids, which comprises passing the acidic hydrolysate in contact with an anion exchange resin. 45 50

2. A process according to claim 1 in which the resin is arranged in a fixed bed and the hydrolysate is contacted with the resin by causing the hydrolysate to flow through the bed until the exchange capacity of the resin is nearly or completely exhausted and the resin is then regenerated by means of an alkali-metal hydroxide solution. 55

3. A process according to claim 2, in which the nearly or completely exhausted resin is first purged with acetone, then washed with demineralised water, and then regenerated with the alkali-metal hydroxide solution. 60

4. A process according to claim 2 in which the nearly or completely exhausted resin is purged with air and then repeatedly flooded with acetone, the acetone is then displaced from the bed by means of demineralised water and the resin in the bed is then regenerated by the alkali metal hydroxide solution. 65 70

5. A process according to any of claims 2 to 4 in which the regenerating solution is displaced from the resin bed first by demineralised water and then by air or acetone. 75

6. A process for neutralising a hydrolysate obtained by the hydrolysis with inorganic acids of a solution of cumene hydroperoxide in cumene containing at least 25% by weight cumene hydroperoxide, substantially as herein described in any of the Examples. 80

A. A. THORNTON & CO.,

Chartered Patent Agents,

Northumberland House,

303—306, High Holborn, London, W.C.1,

For the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1964.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained

